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# New manganese catalysts for alcohol oxidation

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Dedicated to Professor Karl Wieghardt

## Abstract

The in situ prepared manganese complexes based on ligands **1–6** have been used in the catalytic oxidation of alcohols to aldehydes or ketones. Highly active and selective catalysts were found with excellent turnover numbers (up to 900) using aqueous hydrogen peroxide as oxidant at ambient temperatures. EPR spectroscopy and electrospray mass spectrometry has indicated that dinuclear species may be involved in the catalytic oxidations. Comparing the rate of oxidation of benzyl- $d_7$  alcohol with that of benzyl alcohol by the different catalysts yielded isotope effects ( $k_H/k_D$ ) of 2.2–4.3. Although the exact nature of the oxidising species has not been elucidated, these results indicate that hydroxyl radicals are not involved in these processes.

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**Keywords:** Hydrogen peroxide; Oxidation; Alcohols; Manganese complexes

## 1. Introduction

Manganese can frequently be found in the catalytic redox centre of several enzymes like superoxide dismutase [1], catalase [2] and the oxygen evolving complex photosystem II (PS II) [3]. The active site of manganese superoxide dismutases contains a mononuclear five-coordinate Mn(III)-ion. The mechanism of the catalytic conversion of superoxide, a harmful radical for living organisms, to oxygen starts by binding of the superoxide radical anion to the Mn(III)-monomer, which leads to reduction to Mn(II) and oxidation of superoxide into oxygen. Subsequently, the catalytic cycle is closed by binding of a second superoxide to the Mn(II)-ion resulting in the oxidation of Mn(II) and reduction of superoxide anion to hydrogen peroxide ( $H_2O_2$ ). In PS II, located in the thylakoid membrane of chloroplasts in green plants, algae and a number of cyanobacteria, two water molecules are oxidised to dioxygen. PS II consists of light harvesting pigments, a water oxidation centre (WOC), and electron transfer components [3]. Based on

many spectroscopic measurements it has been recognised that a tetranuclear Mn cluster is the active catalyst for the oxygen evolution, which has been recently confirmed by the crystal structure [4]. However, the exact mechanism of the water oxidation has not been elucidated so far. Catalases decompose  $H_2O_2$  to water and oxygen and these Mn enzymes have been isolated from three different bacteria; *Lactobacillus plantarum* [5], *Thermus thermophilus* [6], and *Thermoleophilum album* [2]. X-ray crystallographic structure analysis [7] elucidated that these catalases contain a dinuclear Mn-centre. During the catalytic process the dinuclear Mn active site cycles between the  $Mn_2^{II}$  and  $Mn_2^{III}$  oxidation states [8]. EPR [9], NMR [10] and UV–Vis [10a] spectroscopic studies revealed that for  $H_2O_2$  disproportionation both  $Mn_2^{II}$  and  $Mn_2^{III}$  oxidation states are involved. Many compounds containing a dinuclear Mn core encompassed by a variety of ligand types have been employed as catalase model [11]. Manganese complexes based on 1,4,7-triazacyclononane (tacn) ligands were extensively studied by Wieghardt et al. as enzyme models [12]. Recently, these complexes were also employed as bleaching- [13], epoxidation- [14] and alcohol-oxidation [15] catalysts, using  $H_2O_2$  as oxidant, by us [14d,15] and a number of other research groups [16]. Turnover numbers in the range of 80–1000 were readily

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reached using this oxidant. Hydrogen peroxide shows high atom efficiency since water is the only expected by-product and therefore, it is very attractive for industrial applications. Consequently, the development of novel synthetic methodology based on Mn-catalysed oxidations with  $\text{H}_2\text{O}_2$  is a major challenge. Synthesis and modifications of the tacn ligand are not easily accomplished due to lengthy and tedious preparation, whereas the sensitivity of the corresponding Mn-complexes to changes in the tacn ligand structure often leads to completely inactive Mn-complexes.

In the course of our studies on novel ligands featuring three N-donor sets for each Mn-centre in dinuclear Mn-complexes, we explored the dinucleating ligands [17] *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,2-ethanediamine (tpen, **1**) and *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,3-propanediamine (tptn, **2**, Fig. 1) in catalytic epoxidation reactions [18]. Advantages of this type of ligands are the easy accessibility and the possibility for ligand modification. Screening the corresponding dinuclear Mn-complexes in a number of different catalytic epoxidation reactions showed that the complexes based on tpen (**1**) were unreactive, in sharp contrast to the Mn-complexes based on tptn (**2**), containing a two- or a three-carbon spacer, respectively [18b].

We report here the use of tptn (**2**) and related ligands in Mn-catalysed oxidation of a variety of primary and secondary alcohols with  $\text{H}_2\text{O}_2$  as oxidant. It will be shown that several in situ prepared complexes with  $\text{Mn}(\text{OAc})_3$  based on tptn (**2**) and tptn-derivatives are active and selective catalysts for the oxidation of a number of substituted primary benzyl alcohols to benzaldehydes and secondary alcohols to the corresponding ketones.

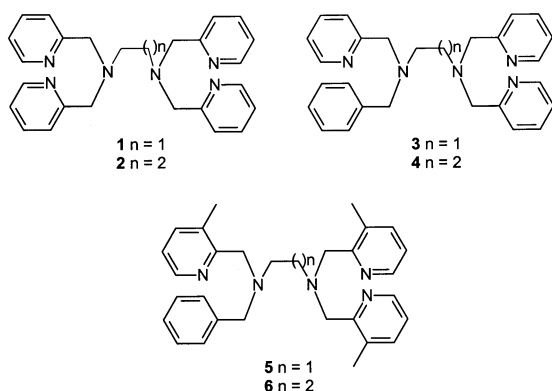


Fig. 1. Ligands used for the Mn-catalysed alcohol oxidation.

## 2. Experimental

### 2.1. Instrumentation

$^1\text{H}$  NMR spectra were recorded on a Varian Gemini-300 (300 MHz) spectrometer. Chemical shifts are denoted in  $\delta$ -units (in ppm) relative to residual solvent peak ( $\text{CHCl}_3 = 7.27$  ppm).  $^{13}\text{C}$  NMR spectra (APT) were recorded on a Varian-300 (75.48 MHz) spectrometer. Chemical shifts are denoted in  $\delta$ -units (in ppm) relative to the solvent and converted to TMS scale using  $\delta(\text{CHCl}_3) = 77.0$  ppm. The splitting patterns are designated as follows: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants,  $J$  are denoted in Hz.

GC analysis were performed on a Hewlett-Packard 6890 Gas Chromatograph equipped with an autosampler, using a HP-1 dimethyl polysiloxane column or a HP-5 5% phenylmethylsiloxane column. Calibration was performed using authentic samples of alcohols and carbonyl compounds. Conversions, yields and turnover numbers were determined using  $\text{C}_6\text{H}_5\text{Br}$  or 1,2-dichlorobenzene as internal standard, and calculated using the Chemstation software.

Mass spectra were obtained on a JEOL JMS-600H mass spectrometer (CI, EI) or a AEI MS-902 mass spectrometer. The electrospray mass experiments were performed at room temperature (r.t.) at a Micromass ZMD 2000, ESIC(+) Vcone = 20 V and Vcap = 3.25 kV connected to a Alliance 2690 HPLC system, at the analytical department of the University of Groningen.

EPR experiments were carried out using a Bruker ECS 106 at 77 K.

### 2.2. Synthesis of ligands

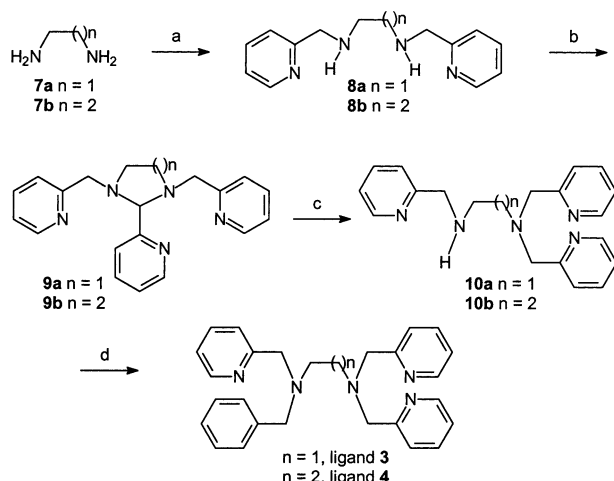
#### 2.2.1. *N,N,N',N'*-Tetrakis(2-pyridinylmethyl)-1,2-ethanediamine (**1**), *N,N,N',N'*-tetrakis(2-pyridinylmethyl)-1,3-propanediamine (**2**)

Ligands **1** and **2** were synthesised according to Ref. [17].

#### 2.2.2. *N*<sup>1</sup>-Benzyl-*N*<sup>1</sup>,*N*<sup>2</sup>,*N*<sup>2</sup>-tris(2-pyridinylmethyl)-1,2-ethanediamine (**3**) and *N*<sup>1</sup>-benzyl-*N*<sup>1</sup>,*N*<sup>3</sup>,*N*<sup>3</sup>-tris(2-pyridinylmethyl)-1,3-propanediamine (**4**)

Ligands **3** and **4** were synthesised according to several (slightly modified) literature procedures [19]. The general route is given in Scheme 1. *N*<sup>1</sup>,*N*<sup>2</sup>-Bis(2-pyridinylmethyl)-1,2-ethanediamine (**8a**) and *N*<sup>1</sup>,*N*<sup>3</sup>-bis(2-pyridinylmethyl)-1,3-propanediamine (**8b**) were synthesised as reported earlier [20].

##### 2.2.2.1. 2-{[2-(2-Pyridinyl)-3-(2-pyridinylmethyl)-1-imidazolidinyl]methyl}pyridine (**9a**). A solution of 3.8 g (15.9 mmol) of **8a** and 1.7 g (15.9 mmol) of 2-pyridinecarboxaldehyde in 10 ml $\text{Et}_2\text{O}$ was stirred at



Scheme 1. Synthesis of ligands **3** and **4**. (a) MeOH, 2-pyridinecarboxaldehyde, NaBH<sub>4</sub>. (b) Et<sub>2</sub>O, 2-pyridinecarboxaldehyde, molecular sieves 4 Å. (c) CH<sub>3</sub>OH, NaBH<sub>3</sub>CN, CF<sub>3</sub>CO<sub>2</sub>H. (d) 1,2-Dichloroethane, benzaldehyde, NaBH(OAc)<sub>3</sub>.

r.t. with CaCl<sub>2</sub> protection. The reaction mixture was stirred for 16 h and the white precipitate was recovered after filtration and washed with Et<sub>2</sub>O to afford **9a** (4.5 g, 13.8 mmol, 86% yield) as the solid product. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.45 (d, 1H, Py, *J* = 5.12 Hz), 8.40 (d, 2H, Py, *J* = 4.76 Hz), 7.83 (d, 1H, Py, *J* = 8.05 Hz), 7.64 (dt, 1H, Py, *J* = 7.69, 1.46 Hz), 7.51 (dt, 2H, Py, *J* = 7.60, 1.59 Hz), 7.29 (d, 2H, Py, *J* = 7.69 Hz), 7.14 (m, 1H, Py), 7.03 (m, 2H, Py), 4.22 (s, 1H, CH), 3.89 (d, 2H, CH<sub>2</sub>, *J* = 14.3 Hz), 3.60 (d, 2H, CH<sub>2</sub>, *J* = 14.3 Hz), 3.26 (m, 2H, CH<sub>2</sub>), 2.69 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz): δ 158.4, 156.6, 146.3, 145.9, 134.2, 133.7, 120.7, 120.5, 120.3, 119.3, 86.7, 56.4, 48.8.

**2.2.2.2. 2-(2-Pyridinyl)-1,3-bis(2-pyridinylmethyl)hexahydropyrimidine (9b).** Compound **9b** was synthesised analogous to compound **9a** starting from 6.0 g (22.8 mmol) of **8b** and 2.4 g (22.8 mmol) of 2-pyridinecarboxaldehyde affording 6.5 g (19.0 mmol) of the product as a white solid (83% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.47 (d, 1H, Py, *J* = 4.76 Hz), 8.36 (d, 2H, Py, *J* = 4.39 Hz), 7.84 (d, 1H, Py, *J* = 8.06 Hz), 7.59 (dt, 1H, Py, *J* = 7.69, 1.46 Hz), 7.50 (dt, 2H, Py, *J* = 7.69, 1.47 Hz), 7.69 (d, 2H, Py, *J* = 7.69 Hz), 7.08 (dt, 1H, Py, *J* = 6.23, 1.47 Hz), 6.99 (t, 2H, Py, *J* = 6.59, 5.86 Hz), 3.99 (s, 1H, CH), 3.53 (d, 2H, CH<sub>2</sub>, *J* = 14.7 Hz), 3.27 (d, 2H, CH<sub>2</sub>, *J* = 14.7 Hz), 2.97 (m, 2H, CH<sub>2</sub>), 2.24 (dt, 2H, CH<sub>2</sub>, *J* = 2.56 Hz), 1.89 (m, 1H, CH<sub>2</sub>), 1.50 (m, 1H, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 162.3, 160.3, 149.0, 148.9, 137.4, 136.8, 124.1, 123.8, 123.1, 122.2, 88.9, 60.5, 52.4, 25.0.

**2.2.2.3. N<sup>1</sup>,N<sup>1</sup>,N<sup>2</sup>-Tris(2-pyridinylmethyl)-1,2-ethanediamine (10a).** To a solution of 1.0 g (3.04 mmol) of amina **9a** in 50 ml MeOH was added 0.19 g (3.02 mmol)

of NaBH<sub>3</sub>CN and 0.46 ml (5.98 mmol) of CF<sub>3</sub>CO<sub>2</sub>H. The solution was stirred at r.t. with CaCl<sub>2</sub> protection for 18 h. A 15% NaOH solution (30 ml) was added and after stirring for 3 h the solution was extracted with 3 × 50 ml of CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation of the solvent afforded 0.70 g (2.13 mmol) of **10a** (70% yield) as a yellow oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.46 (m, 3H, Py), 7.52 (m, 5H, Py), 7.16 (m, 4H, Py), 3.75 (s, 6H, 3 × CH<sub>2</sub>), 2.70 (s, 4H, 2 × CH<sub>2</sub>), 2.40 (br, 1H, NH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 157.5, 157.1, 146.7, 146.4, 133.8, 133.7, 120.7, 120.4, 119.4, 119.2, 58.1, 52.5, 51.6, 44.2. HRMS Calc. for C<sub>20</sub>H<sub>23</sub>N<sub>5</sub>: 333.195. Found: 333.196.

**2.2.2.4. N<sup>1</sup>,N<sup>1</sup>,N<sup>3</sup>-Tris(2-pyridinylmethyl)-1,3-propanediamine (10b).** Compound **10b** was synthesised analogous to compound **10a** starting from 1.0 g (2.92 mmol) of **9b**, 0.18 g (2.90 mmol) of NaBH<sub>3</sub>CN and 0.44 ml (5.74 mmol) of CF<sub>3</sub>CO<sub>2</sub>H to afford 0.74 g (2.13 mmol) of product as a yellow oil (73% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.44 (m, 3H, Py), 7.49 (m, 5H, Py), 7.11 (m, 4H, Py), 3.77 (s, 2H, CH<sub>2</sub>), 3.72 (s, 4H, 2 × CH<sub>2</sub>), 2.56 (m, 4H, 2 × CH<sub>2</sub>), 1.95 (br, 1H, NH), 1.71 (q, 2H, CH<sub>2</sub>, *J* = 6.95 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 157.5, 157.3, 146.7, 146.4, 133.8, 120.3, 119.6, 119.3, 57.9, 52.9, 50.0, 45.4, 24.9. HRMS Calc. for C<sub>21</sub>H<sub>25</sub>N<sub>5</sub>: 347.210. Found: 347.211.

**2.2.2.5. N<sup>1</sup>-Benzyl-N<sup>1</sup>,N<sup>2</sup>,N<sup>2</sup>-tris(2-pyridinylmethyl)-1,2-ethanediamine (3).** To 0.70 g (2.10 mmol) of **10a** in 25 ml of 1,2-dichloroethane was added 0.24 g (2.31 mmol) of C<sub>6</sub>H<sub>5</sub>CHO. During 1 h 1.34 g (6.29 mmol) of NaBH(OAc)<sub>3</sub> was added in small portions. After stirring for 24 h at r.t. 30 ml of a saturated solution of NaHCO<sub>3</sub> was added, followed by extraction with 3 × 50 ml CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), the solvent evaporated under reduced pressure to afford the crude product. The oil was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, akt. II–III, EtOAc/C<sub>6</sub>H<sub>14</sub>/Et<sub>3</sub>N 10:4:1) to afford 0.31 g (0.73 mmol) of the pure product as a yellow oil (35% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.42 (m, 2H, Py, 1H, Ar), 7.51 (m, 3H), 7.39 (m, 3H), 7.19 (m, 5H), 7.05 (m, 3H), 3.70 (s, 4H, 2 × CH<sub>2</sub>), 3.65 (s, 2H, CH<sub>2</sub>), 3.52 (s, 2H, CH<sub>2</sub>), 2.66 (m, 4H, 2 × CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 157.0, 157.3, 146.5, 146.3, 136.7, 133.8, 126.2, 125.7, 124.4, 120.2, 120.1, 119.3, 119.2, 58.3, 58.1, 56.2, 49.8, 49.4. HRMS Calc. for C<sub>27</sub>H<sub>29</sub>N<sub>5</sub>: 423.242. Found: 423.242.

**2.2.2.6. N<sup>1</sup>-Benzyl-N<sup>1</sup>,N<sup>3</sup>,N<sup>3</sup>-tris(2-pyridinylmethyl)-1,3-propanediamine (4).** Compound **4** was synthesised analogous to compound **3** starting from 0.74 g (2.07 mmol) of **10b**, 0.24 g (2.31 mmol) of C<sub>6</sub>H<sub>5</sub>CHO and 1.34 g (6.29 mmol) of NaBH(OAc)<sub>3</sub> to afford 0.48 g (1.10 mmol) of the product after purification by column chromatography (Al<sub>2</sub>O<sub>3</sub>, akt. II–III, EtOAc/C<sub>6</sub>H<sub>14</sub>/

Et<sub>3</sub>N 10:2:1) as a yellow oil (yield 53%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.42 (m, 3H), 7.52 (m, 3H), 7.34 (d, 3H, *J* = 8.06 Hz), 7.17 (m, 5H), 7.04 (m, 3H), 3.69 (s, 4H, 2 × CH<sub>2</sub>), 3.61 (s, 2H, CH<sub>2</sub>), 3.61 (s, 2H, CH<sub>2</sub>), 2.49 (t, 2H, CH<sub>2</sub>, *J* = 7.69, 6.95 Hz), 2.41 (t, 2H, *J* = 7.32, 6.96 Hz), 1.72 (q, 2H, CH<sub>2</sub>, *J* = 7.32, 6.96 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 157.8, 157.4, 146.4, 146.2, 136.9, 133.8, 126.3, 125.6, 124.3, 120.3, 120.2, 119.3, 119.2, 57.9, 57.6, 56.1, 49.9, 49.4, 22.1. HRMS Calc. for C<sub>28</sub>H<sub>31</sub>N<sub>5</sub>: 437.258. Found: 437.257.

2.2.2.7. *N*<sup>1</sup>-Benzyl-*N*<sup>1</sup>,*N*<sup>2</sup>,*N*<sup>2</sup>-tris[(3-methyl-2-pyridinyl)methyl]-1,2-ethanediamine (**5**), *N*<sup>1</sup>-benzyl-*N*<sup>1</sup>,*N*<sup>3</sup>,*N*<sup>3</sup>-tris[(3-methyl-2-pyridinyl)methyl]-1,3-propanediamine (**6**). Ligands **5** and **6** were synthesised according to Ref. [21].

### 2.3. Catalytic oxidation experiments

Catalytic alcohol oxidation reactions were started by mixing 1.0 ml of a stock solution of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O in C<sub>3</sub>H<sub>6</sub>O and 1.0 ml of a stock solution of ligand **2** (or **1**). After stirring for 15 min 1.0 ml of a stock solution of substrate and C<sub>6</sub>H<sub>5</sub>Br (internal standard) were added. After stirring for 2 min, excess of H<sub>2</sub>O<sub>2</sub> (1.0 ml of 30% aq. H<sub>2</sub>O<sub>2</sub>) was added. The concentrations of Mn(OAc)<sub>3</sub>, ligand **2** (or **1**), substrate, H<sub>2</sub>O<sub>2</sub> and internal standard were 2 mM, 1 mM, 1 M, 9.8 M and 0.5 M, respectively.

The progress of the reaction was monitored by GC, by taking a small sample of the reaction mixture and filtering over a short column of silica. To establish the identity of the alcohols and carbonyl compounds unequivocally, the retention times and spectral data were compared to those of commercially available or independently synthesised compounds. The same procedure as described for the catalytic reactions with **2** was followed with ligands **3**–**6** except that the concentration of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O was now 1 M to yield a Mn–ligand of 1:1. Besides the use of a range of alcohols, also benzene which can act as a hydroxyl radical trap [29], was applied as substrate under similar reaction conditions as previously described.

#### 2.3.1. Determination of the primary kinetic isotope effect (*k<sub>H</sub>/k<sub>D</sub>*) for the oxidation of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH and benzyl-*d*<sub>7</sub> alcohol

The same procedure as described for the catalytic oxidation experiments (Section 2.3) was followed except that 1.0 ml of a stock solution (conc. 1 M) of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH, *p*-methylbenzyl alcohol and of C<sub>6</sub>H<sub>5</sub>Br (conc. 0.5 M, internal standard) were used. Another solution, using benzyl-*d*<sub>7</sub> alcohol, *p*-methylbenzyl alcohol and C<sub>6</sub>H<sub>5</sub>Br (internal standard), was also prepared and used as substrate. The amounts of alcohols before and after the oxidation reaction with H<sub>2</sub>O<sub>2</sub> were determined by GC analysis. The *k<sub>H</sub>/k<sub>D</sub>* value was

determined using the following equations [22]:

$$k_H/k_{Me} = \log(H_f/H_i)/\log(Me_f/Me_i) \quad (1)$$

$$k_D/k_{Me} = \log(D_f/D_i)/\log(Me_f/Me_i) \quad (2)$$

then,

$$k_H/k_D = \text{Eq. (1)}/\text{Eq. (2)}$$

*H<sub>f</sub>* and *H<sub>i</sub>* are final and initial quantities of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH. *D<sub>f</sub>* and *D<sub>i</sub>* are final and initial quantities of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH-*d*<sub>7</sub>. *Me<sub>f</sub>* and *Me<sub>i</sub>* are final and initial quantities of *p*-methylbenzyl alcohol.

## 3. Results and discussion

Data for the conversions of various alcohol substrates to the corresponding carbonyl compounds are summarised in Table 1. The in situ prepared Mn-catalyst based on ligand **1** resulted in a unreactive oxidation catalyst. However, the in situ prepared Mn-catalyst based on ligand **2** (Fig. 1) provided in a highly active and selective alcohol oxidation catalyst. The conversion of benzyl alcohol (entry 1) resulted in the selective formation of benzaldehyde with 326 tons. Remarkably, Mn-catalyst **2** seems almost not affected by the nature of the *para*-substituents achieving high tons in the range of 201 (4-methoxybenzyl alcohol, entry 2)–449 (4-chlorobenzyl alcohol, entry 3). Although substrates with electron donating properties e.g. 4-methoxybenzyl alcohol (entry 2) reacts less efficient compared to substrates containing electron-withdrawing groups like 4-trifluoromethyl benzyl alcohol (entry 4) rather small effects on the catalysis were found. However, a distinct steric effect was observed as *ortho*-substituted substrates react more sluggish and in fact 2,5-dimethoxybenzyl alcohol (entry 6) was found to be virtually unreactive. As in the case of primary alcohol substrates, high conversions were obtained for the oxidation of secondary alcohols. For example, the oxidation of cyclohexanol (entry 7) resulted in 363 tons and also for cycloheptanol (entry 8) excellent results (894 tons) were found with selectivities up to 99%. In some cases lower selectivities were observed (i.e. entry 4, 4-trifluoromethyl benzyl alcohol). Perhaps overoxidation to benzoic acid takes place, however this was not quantified. Other secondary alcohols like 2-octanol (entry 10) and *sec*-phenylethylalcohol (entry 11) were selectively transformed to the corresponding ketones with satisfactory conversions. Although the oxidation of secondary alcohols proceeds with high conversions, the in situ prepared complexes gave only low conversions in the oxidation of 1-octanol (entry 9).

The Mn-complex prepared in situ using ligand **3** (Fig. 1) resulted in dramatic lower tons for the oxidation of the range of the substrates. With the substituted benzyl alcohols (entries 1–6) only low tons were reached,



Table 1

Oxidation of selected alcohols with in situ prepared Mn-catalysts based on ligands 2–6<sup>a</sup>

Substrate <sup>b</sup>	Turnover numbers after 4 h (ton) <sup>c</sup> and selectivity (%) with ligands 2–6									
	2	Selectivity <sup>d</sup>	3	Selectivity <sup>d</sup>	4	Selectivity <sup>d</sup>	5	Selectivity <sup>d</sup>	6	Selectivity <sup>d</sup>
Benzyl alcohol	326	95	127	95	293	95	331	99	303	99
4-Methoxybenzyl alcohol	201	80	97	80	255	80	270	75	291	75
4-Chlorobenzyl alcohol	449	99	127	99	308	99	392	99	414	99
4-Trifluoromethyl benzyl alcohol	329	70	173	90	352	90	317	70	258	70
4-Fluorobenzyl alcohol	233	90	21	99	231	88	240	80	248	70
2,5-Dimethoxybenzyl alcohol	90	99	63	99	72	99	71	99	63	99
Cyclohexanol	363	95	486	80	595	70	583	85	593	80
Cycloheptanol	849	85	735	90	894	90	808	99	688	99
1-Octanol	108	85	53	85	63	70	53	90	46	90
2-Octanol	680	95	298	95	555	95	664	85	480	95
sec-Phenylethyl alcohol	657	90	400	70	593	70	793	90	715	95

<sup>a</sup> Experimental conditions, see Section 2.2.<sup>b</sup> All products were identical to independent samples and identified by GC (HP 6890, column HP1 15 × 0.3 mm × 2.65 μm, polydimethylsiloxane) and <sup>1</sup>H NMR.<sup>c</sup> Turnover number—mole product per mole ligand.<sup>d</sup> Selectivity in mole aldehyde (or ketone) per mole converted substrate.

typically between 21 (entry 5) and 173 (entry 4), whereas employing secondary alcohols generally higher conversions were observed. Higher tons were reached by using the in situ prepared complex of ligand 4, containing a three-carbon spacer, and the observed results are comparable with the initial used Mn-complex based on ligand 2. Suitable oxidation catalysts were also found by employing the Mn-complexes based on ligands 5 and 6, resulting in high conversions and selectivities for primary and secondary alcohols. Generally the results even surpasses those results found for ligand 2, achieving turnover numbers easily over 700.

Addition of a second amount of H<sub>2</sub>O<sub>2</sub> (1 ml of a 30% solution in water) resulted in some cases in a considerable increase in aldehyde or ketone yield, indicating that the catalysts are robust under the conditions used. In a control experiment in which the ligand was omitted, strong peroxide decomposition and no oxidation products were found. In the absence of the Mn salt only substrate and no oxidation products were found.

The reaction time profiles were followed for the oxidation of cyclohexanol to cyclohexanone and the results are summarised in Fig. 2. Turnover numbers up to 600 were easily reached for the Mn-complexes. Following the time course of the oxidation of cyclohexanol, a remarkable decrease in induction time was obtained for the complexes based on ligands 5 and 6, containing additional methyl groups at the 3-position of the pyridine rings, compared to the Mn-complexes based on ligands 3 or 4. The striking influence of the additional methyl groups on the reactivity could be a result of either electronic or steric properties of the ligands; perhaps pointing to a change in coordination of the ligand as has been observed for Fe–tpa complexes (tpa = *N,N,N*-tris(2-pyridinylmethyl)amine [23]. How-

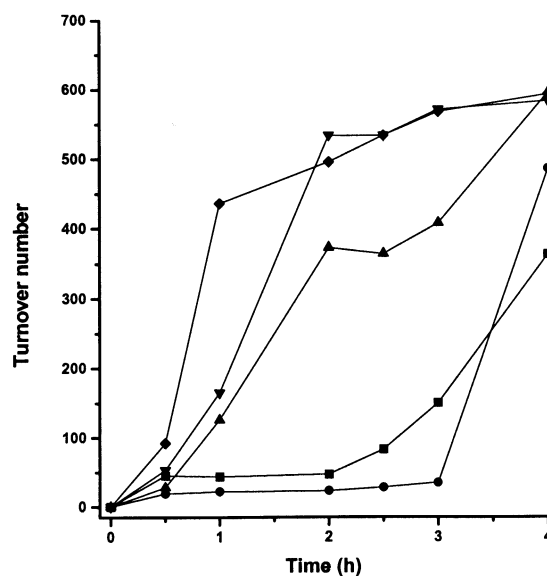


Fig. 2. Time profile of the oxidation of cyclohexanol with Mn-complexes prepared in situ with ligands 2–6: ■, 2; ●, 3; ▲, 4; ▼, 5; ◆, 6.

ever, additional research is necessary to elucidate the origin of these effects and to establish the relation between the methyl groups in the ligands and the observed enhanced reactivity.

The primary kinetic isotope data obtained for many alcohol oxidation reactions by high-valent transition metal complexes usually indicate the involvement of an association/dissociation equilibrium of the alcohol to the metal complex prior to hydride or hydrogen transfer [24]. The primary kinetic isotope effect ( $k_H/k_D$  for the Mn-catalysed oxidation of benzyl alcohol and benzyl-*d*<sub>7</sub> alcohol observed are in the range of 2.2–4.3 (ligand 2,

3.2; ligand **3**, 2.2; ligand **4**, 4.3; ligand **5**, 3.1; ligand **6**, 3.4). These values strongly indicate that cleavage of the (benzylic) C–H bond is involved in the rate-determining step [25]. Slightly higher values were found for the Cu-based galactose oxidase models studied by the groups of Stack ( $k_H/k_D = 5.3$ ) [26] and Itoh ( $k_H/k_D = 6.8$ ) [26]. A primary kinetic isotope value of 7.7 was found for galactose oxidase itself by Maradufu et al. [27]. Similar values ( $k_H/k_D = 4.0$ ) were found in our group for the oxidation of primary and secondary alcohols using a non-heme dinuclear iron catalyst [28]. Based on these experiments it can be concluded that hydroxyl radicals are not involved in these processes, as due to the high reactivity of these radicals a much lower isotopic effect would be expected [28]. In agreement, no indications for hydroxylation of aromatic rings for the various substrates employed as listed in Table 1 have been obtained. Furthermore, no hydroxylation of benzene under the same conditions has been observed which is also a substrate sensitive to hydroxylation [29].

### 3.1. EPR and ES/MS experiments

The catalytic alcohol oxidation reactions were investigated by electron paramagnetic resonance spectroscopy (EPR). Initial experiments involved the in situ preparation of the Mn-complexes using ligands **1–6** (Fig. 2, for catalytic oxidation details, see Section 2.3). Samples of the catalytic oxidation reaction mixture at 0 °C were taken in acetone and frozen to 77 K for EPR studies. After mixing the ligands and  $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$  for 15 min no EPR signals were obtained at 77 K, which may be caused by the formation of EPR-silent Mn(III) or Mn(IV)Mn(IV) species.

After addition of substrate (cyclohexanol) and oxidant (1.0 ml of 30% aq.  $\text{H}_2\text{O}_2$ ) samples were immediately frozen to 77 K for EPR analysis. The EPR spectrum displayed a weak 16-line signal for the complexes based on ligands **2** and **4** whereas for the complexes based on ligands **3** and **5** no EPR signals were detected. However, the in situ prepared complex with ligand **6** results in a strong 16-line signal immediately after addition of oxidant (Fig. 3). After 90 min incubation at 0 °C strong signals were obtained for in situ prepared complexes based on ligands **2–6** in the presence of  $\text{H}_2\text{O}_2$ , which represent characteristic 16-line spectra for mixed-valence Mn(III)Mn(IV) complexes with an  $A$  value of 78 G [30]. After a reaction period of 4 h, however, only the complexes based on ligands **2** and **3** still displayed a weak Mn(III)Mn(IV) EPR signal (roughly 10% of the intensity observed after 90 min). The Mn-complexes based on ligands **3–5** showed a six line EPR signal with an  $A$  value of 108 G, typical for a mononuclear Mn(II) species. In sharp contrast to the Mn-complexes based on ligands **2–6**,

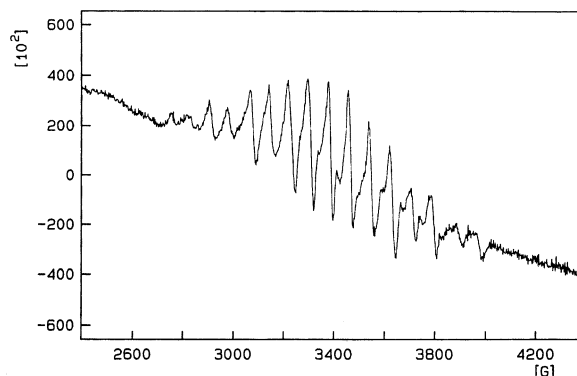


Fig. 3. Electron paramagnetic resonance spectrum of in situ prepared Mn-complex based on ligand **6** immediately after addition of cyclohexanol and oxidant.

ligand **1** (tpen) remained EPR silent over a 4 h reaction period.

Attempts to monitor the oxidation reactions with electrospray mass spectroscopy (ES/MS) resulted in the observation of mainly mononuclear complexes after mixing the ligands **1–6** with  $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ . Upon mixing ligand **1** with the Mn salt, the ES/MS spectrum showed prominent peaks at  $m/z$  425 and 538, corresponding to protonated ligand **1** ( $[\text{HL}]^+$ ) and a mononuclear complex identified as  $[\text{LMn}(\text{OAc})]^+$ , respectively. Similar species were obtained by preparing the complex in situ from ligand **2**, resulting in signals at  $m/z$  439 and 552. Although after mixing ligand **3** with  $\text{Mn}(\text{OAc})_3$  signals for mononuclear complexes ( $m/z$  537) were observed, using ligand **4** containing a three-carbon spacer, a base peak of  $m/z$  438 was found which was assigned to the free ligand. However, mixing ligands **5** and **6** resulted in peaks at  $m/z$  579 and 593 assigned to mononuclear species with the general structure  $[\text{LMn}(\text{OAc})]^+$ .

After addition of substrate and  $\text{H}_2\text{O}_2$  to the in situ prepared Mn-complexes we found for the complex based on ligand **1** a base peak (at  $m/z$  538), which was assigned to  $[\text{LMn}(\text{OAc})]^+$ . In contrast for the complexes based on ligands **2**, **4** and **6** signals at  $m/z$  683, 682 and 724 were detected, corresponding to species like  $[\text{LMn}_2^{\text{II}}(\text{OAc})_2(\text{OH})]^+$ . It is noted that this is *not* the species observed with EPR. Whilst most Mn(III)Mn(IV) species studied till date are strongly coupled due to two oxygen bridges, dinuclear Mn(II)-complexes with acetato bridges exhibit weak coupling and consequently very different EPR spectra [12]. Although EPR experiments showed also dinuclear complexes after mixing ligands **3** and **5** with  $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ , these results could not be confirmed by the ES experiments.

However, we tentatively propose that by mixing the ligands with Mn salts, subsequent addition of  $\text{H}_2\text{O}_2$  give rise to the formation of dinuclear Mn species, that could be the immediate precursors of the active intermediates for the oxidation of alcohols. During the oxidation

reactions, these complexes are ultimately converted to unreactive mononuclear Mn(II) species.

#### 4. Conclusions

In conclusion, we have demonstrated that the in situ prepared Mn-complex based on tptn (ligand **2**) is a promising catalyst in alcohol oxidation procedures using  $\text{H}_2\text{O}_2$  as the terminal oxidant. Main advantages of this catalytic system are the facile synthesis and possibility for ligand modification. In acetone and at ambient temperature the Mn-complex of tptn is able to catalyse the selective oxidation of various alcohols to the corresponding aldehydes or ketones, with  $\text{H}_2\text{O}_2$  as oxidant. For the selected in situ prepared Mn-complexes based on the discussed ligands, generally turnover numbers up to nearly 900 turnover numbers were found. Preliminary screening in a number of different catalytic alcohol oxidation reactions showed that the in situ prepared Mn-complex with the tpen (**1**) was unreactive, similar to ligand characteristics in previously described epoxidation studies. The tptn based modified ligands **3** and **4**, containing two- and three-carbon spacer, respectively, were found to be moderate (complex based on ligand **3**) to active catalyst (based on ligand **4**), however long induction periods were observed. Using in situ prepared complexes based on ligands **5** and **6** excellent results were found and most remarkably, the induction period was strongly reduced. This may be linked with the observation that ligand **6** yields a strong 16-line EPR signal immediately after mixing the ligand with Mn salt,  $\text{H}_2\text{O}_2$  and substrate and therefore dinuclear species are most probably involved in the oxidation reactions. The ligands with the three-carbon spacer yield in all cases much quicker reactivity (shorter lag phases) than the two-carbon analogues, likely connected with a faster formation of dinuclear species. Based on these studies, however, we cannot conclude which species exactly is involved in the oxidation reactions, i.e. high-valent Mn=O or Mn–OOH species. Further studies towards the elucidation of the mechanism is in progress.

#### 5. Supplementary material

The material is available from the authors on request.

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